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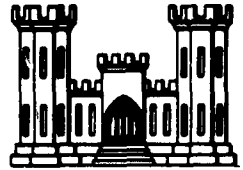
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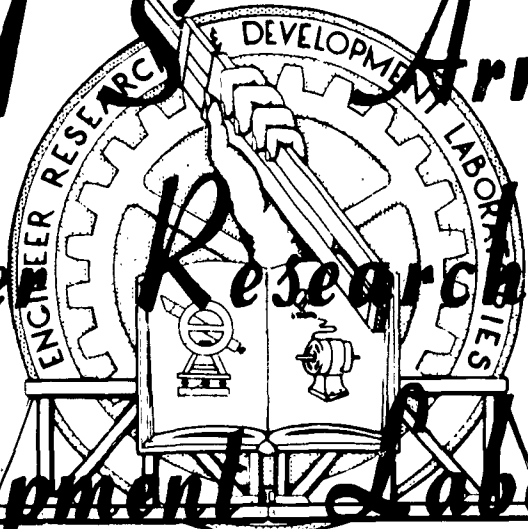
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Use of neutralizing compounds in diesel  
engines operating on sulfur-rich fuel

10 pp

*U S Army  
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FORT BELVOIR, VIRGINIA

USE OF NEUTRALIZING COMPOUNDS IN DIESEL  
ENGINES OPERATING ON SULFUR-RICH FUEL

E-826

T-10

by

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USE OF NEUTRALIZING COMPOUNDS IN DIESEL ENGINES OPERATING ON  
SULFUR-RICH FUEL

It has been proposed to add alkali-metal salts of weak organic acids and other compounds such as zinc naphthenate, colloidal copper, and organic phosphites and amines to high-sulfur fuels in order to combat the corrosive oxides of sulfur (1). It is supposed that the last give rise to basic compounds of nitrogen that bind the oxides (2). There have recently been many publications in the foreign literature on additives for high-sulfur fuels (7), and it appears that most of these additives are complex mixtures of aromatic hydrocarbons (often homologs of naphthalene) with various amines or organometallic compounds very soluble in the fuel (1).

We have made prolonged engine tests on diesel oil containing 1.25% sulfur, to which we added 0.5 - 0.8% of a mixture of organic amines containing 11 - 14% nitrogen. We have found that the amines reduce the corrosion-induced wear and the deposition of gums, but the method is not of great practical value, because these amines (as other additives) are effective only when they are used at the rate of 0.8 - 1.0%, which is far too high. On the other hand, it is obvious that the  $\text{NH}_2$  group is the essential part of the molecule, so we have proposed to introduce directly into the intake either ammonia or ammonium salts\*. The first tests were made in 1956 on a 1Ch-10.5/13 engine with fuel containing 1.25% sulfur; to the intake was admitted a 20% aqueous solution of ammonium carbonate to give  $(\text{NH}_4)_2\text{CO}_3$  to the extent of 0.03% of the fuel. This technique gave very good results; the wear was reduced by a factor 2-3, and the deposition of gums was entirely inhibited. These tests were repeated on other engines with fuels containing up to 1.6% sulfur in conjunction with gaseous ammonia, which was admitted to the induction system in amounts ranging from 0.08 to 0.16% of the weight of the fuel.

Note\*: Author's certificate No. 115 811 issued by the Committee on Inventions and Discoveries in accordance with application No. 571 916 of April 25, 1957.

Figure 1 shows the results for a 2Ch-8.5/11 engine fitted with radioactive piston rings and operating on fuel with 1.6% sulfur; 0.08% ammonia reduced the wear to the level found with low-sulfur fuel. The most effective oil additives (MNIIP-22 and VNII NP-360) had to be added to the oil at the rate of 10-12 wt.% to produce this result. If we assume that the oil consumption is 5% of the fuel consumption, this is equivalent to 0.5 - 0.6 wt.% of the fuel, i.e. 6-7 times more than for ammonia.

Figure 1: Mean wear of the piston rings in 1 hr for a 2Ch-8.5/11 engine.

1 -  $\text{NH}_3$ ; 2 - DS GOST 4749-49; 3 - VNII NP-360; 4 - MNI IP-22K; 5 - TsATIM-339.

Ordinate: Count/min; Abscissa:  
(top) Additive in oil, %; (bottom)  
Additive in fuel, %.

Figure 2: Wear of the piston rings in a 2Ch-8.5/11 engine operating on AS-9.5 oil and on fuel containing 1.57% of sulfur with various additives.

1 - Ammonia in fuel, no additive in oil; 2 - Fuel as in GOST 4749-49, no additive in oil; 3 - Oil with 6% of VNII NP-360; 4 - Oil with 3% of DF-1; 5 - Oil with 3% of TsIATIM-339; 6 - No Additive in oil.

Ordinate: Count/min; Abscissa: Running time, min.

Figure 2 shows the wear rate found with AS-9.5 oil with and without various additives (in every case with ammonia). Similar results were obtained with IT-9-3 and 1Ch10.5/13 engines; the ammonia reduced the formation of gums and deposits, and completely

prevented ring sticking. The effect of 0.16% ammonia is even better (Fig. 1). Recently completed tests with 3D-6 and M-50F engines operating on fuels containing 1.20 and 1.57% ammonia have confirmed these results (Tables 1 and 2). Tests lasting 600 hours each have been performed at TsNII MPS on a 2D-100 engine operating with fuel containing 1.1% sulfur and fed with 0.14% ammonia; these also gave good results (Tables 3 and 4). In fact, gaseous ammonia is a novel and highly effective additive for high-sulfur fuels. It is advantageous to add ammonia to fuels containing over 1% of sulfur for the M 50F and 2D-100 engines even when the oil contains the normal TsIATIM-339 additive.

Table 1: Mean wear of the main parts of a 3D-6 engine after 500 hours.

Part	Operating on		
	1.25% S in fuel, 3% of TsIATIM-339 in oil	1.2% S in fuel with 0.16% $\text{NH}_3$ , oil without additives	1.57% S in fuel with 0.16% $\text{NH}_3$ , oil without additives
Piston	0.078	0.034	0.021
Cylinder liners	0.026	0.011	0.027
Big ends	0.008	0.004	-
Little ends	0.006	0.004	-
Piston rings			
a) mean loss in wt.	0.170	0.077	0.080
b) mean increase in gap (mm)	0.120	0.110	0.100
c) loss of elasticity (kg)	0.210	0.050	0.130

In the early tests with amines the assumption was that these, being basic, would neutralize  $\text{SO}_2$ ,  $\text{SO}_3$ , and other such acid products directly. It is very likely that this is so for amines added to the oil, because the amines come in contact with the combustion products at the surface of the thin film of oil on the walls of the cylinder. It is very doubtful whether any such reaction can occur in the combustion zone, where the temperature rises to 1600°. The exhaust gases show no trace of ammonia or ammonium compounds

when ammonia or ammonium carbonate is added to the air intake. Clearly, the  $\text{NH}_3$  is attacked in the combustion process, although its effect appears as a fall in the proportion of  $\text{SO}_3$  and an increase in the proportion of  $\text{SO}_2$  (Figs. 3 and 4). This change in the balance between  $\text{SO}_3$  and  $\text{SO}_2$  is responsible for the reduction in the wear and for the inhibition of gum formation.

Figure 3:  $\text{SO}_2$  and  $\text{SO}_3$  contents of exhaust gases from a 1Ch-10.5/13 engine.

a - Fuel 1.6% S, no  $\text{NH}_3$ ; b - Fuel 1.6% S,  $\text{NH}_3$  3 liters per hr;

1)  $\text{SO}_2$ ; 2)  $\text{SO}_3$ ; 3)  $\text{SO}_2 + \text{SO}_3$ .

Ordinate:  $\text{SO}_2$  or  $\text{SO}_3$  content, mg in 150 liters; Abscissa: load  $N_e$

Figure 4:  $\text{SO}_2$  and  $\text{SO}_3$  contents of exhaust gases from a 2Ch-8.5/11 engine.

a - Fuel 1.25% S, no  $\text{NH}_3$ ; b - Fuel 1.25% S,  $\text{NH}_3$  3 liters per hour.

1)  $\text{SO}_2$ ; 2)  $\text{SO}_3$ ; 3)  $\text{SO}_2 + \text{SO}_3$

Ordinate:  $\text{SO}_2$  or  $\text{SO}_3$  content, mg in 150 liters; Abscissa: load  $N_e$

The processes responsible for the gum and other deposits are in part accelerated by  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ ; they may be divided roughly into two types.

Table 2: Wear of the main parts of an A-50-P engine

Part	Operating on	
	1.2% S and 0.15% NH <sub>3</sub> in fuel, M-22 oil with 3% of TsIATIM-339	Sulfur-free fuel and M-22 oil
Cylinder liners	0.027	0.037
Pistons	0.038	0.045
Mean increase in gap in piston rings	0.06	0.10
Big ends	0.0026	0.0030
Big-end bearing liners	0.021	0.015
Little ends	0.0023	0.003
Little-end bushing	0.010	0.008
Bushing in Piston	0.017	0.018

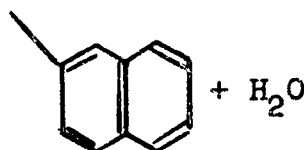
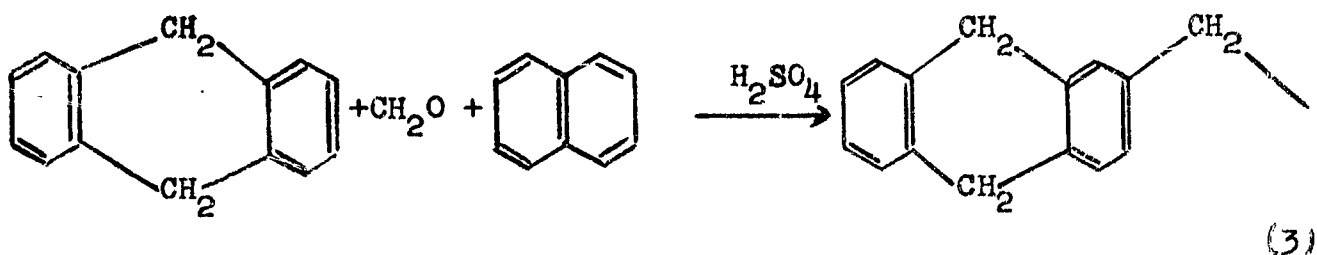
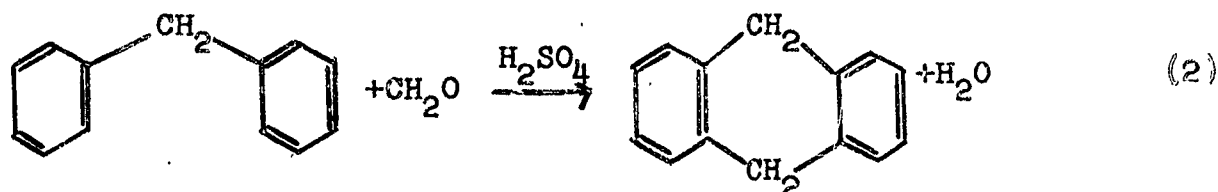
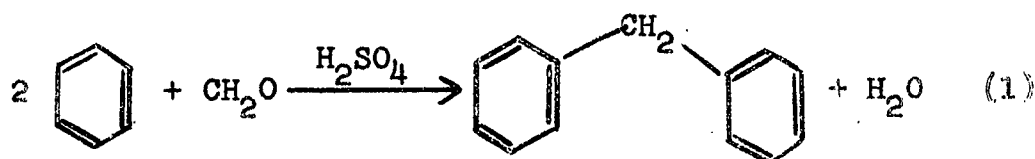
Table 3: Wear of the main parts of a 2D-100 engine after 600 hours.

Part	Wear limits	Fuel GOST 305-58, 1.1% S	
		Oil DSp-11, GOST 8581-57	with 0.14% NH <sub>3</sub> oil DSp-11, GO 8581-57
Wear at skirt (mm)	upper	0.043	0.035
	lower	0.051	0.036
Increase in gap in first compres- sion rings	upper	0.990	0.800
	lower	0.625	0.305
Radial wear of first compression rings at point 1	upper	0.510	0.330
	lower	0.240	0.160
Loss of weight in first compression rings	upper	8.120	6.850
	lower	4.550	3.390
Wear in little end (mm)	rod	0.033	0.028
	bushing	0.009	0.009

Table 4: Formation of gum and deposits in 2D-10 engines after 600 hours.

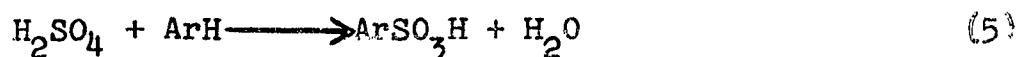
Amount of deposit and state of rings	with $\text{NH}_3$	without $\text{NH}_3$
Amount of deposit in exhaust manifold, g	1558	2146
Amount of deposit in exhaust ports, g	575	1018
Weight of deposits in centrifuge, g	1025	2080
Piston rings (number):		
burned	1	9
stuck	-	4

1. Condensations involving aromatic hydrocarbons, aldehydes, and peroxides, as in NASTYUKOV'S scheme (3, 4):

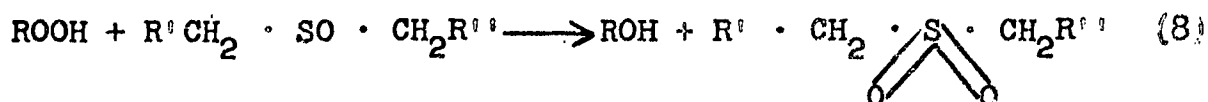
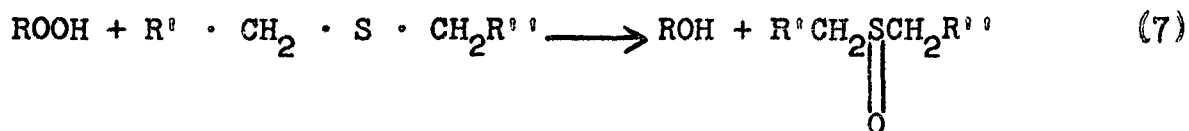


These naphthenic products readily oxidize and condense further to give macromolecular heterocyclic compounds.

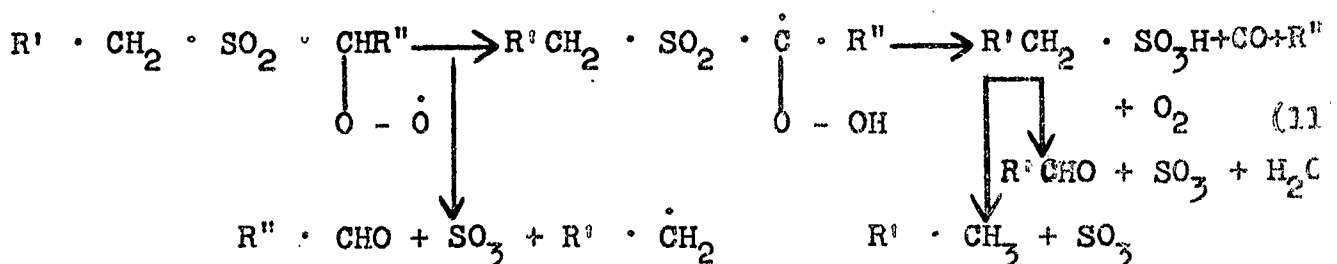
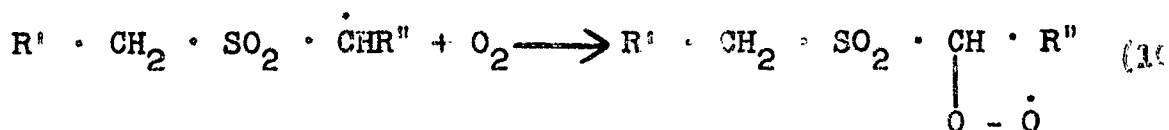
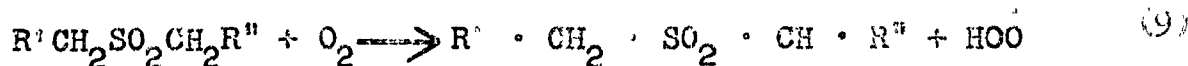
2. Formation of diarylsulfones by reaction between an aromatic hydrocarbon and  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$ :



We have isolated sulfonic acids in the liquid-phase oxidation of sulfur-rich diesel fuels (5); the concentration is a linear function of the sulfur content. For example, the deposit from such oxidation of Tuymazin diesel fuel (1% sulfur) contains a considerable proportion of compounds having the general formula  $\text{C}_n\text{H}_{2n-6} \cdot \text{SO}_2$  (5), which shows that sulfonic acids (i.e. ultimately  $\text{SO}_3$ ) are responsible for much of the sludge and gum in engine oil. On this basis we would expect that measures to eliminate these deposits are dependent largely on reactions that prevent the formation of  $\text{SO}_3$ . Figures 3 and 4 indicate that ammonia retards the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , which process makes a considerable demand for energy and is usually operated in the presence of catalysts. The combustion of sulfides (the major compounds of sulfur in the fuel) in an engine readily gives rise to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , but in the liquid state the sulfides give rise to sulfonic acids and sulfones:

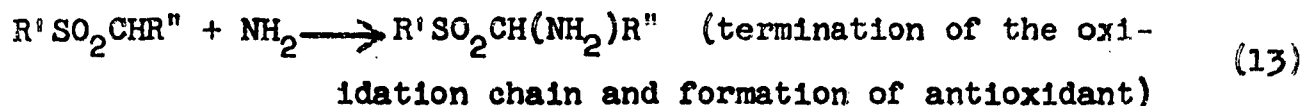
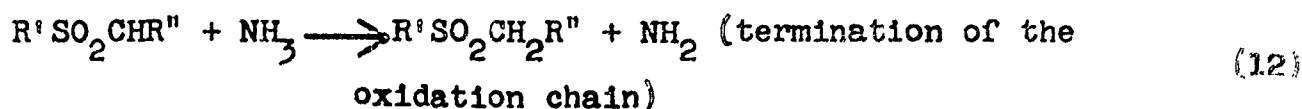


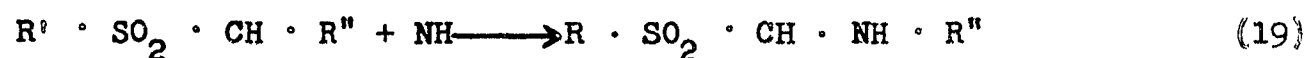
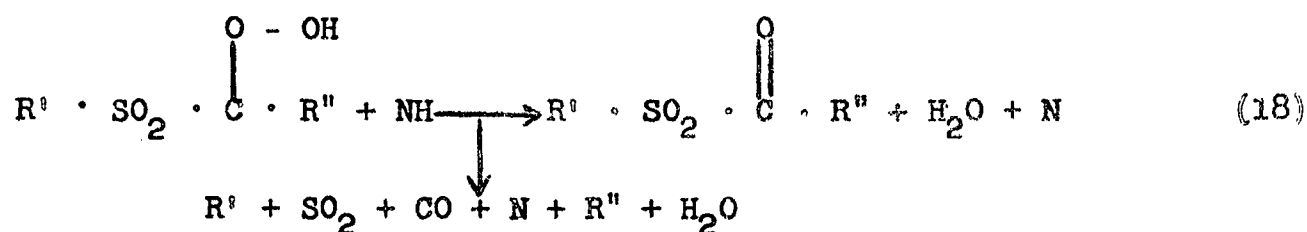
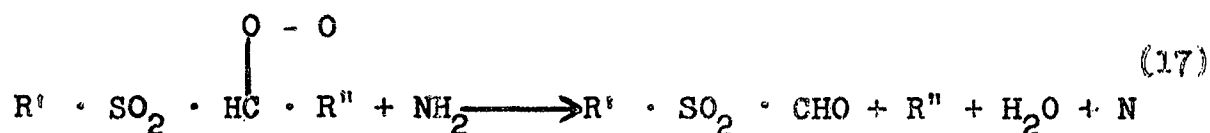
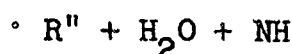
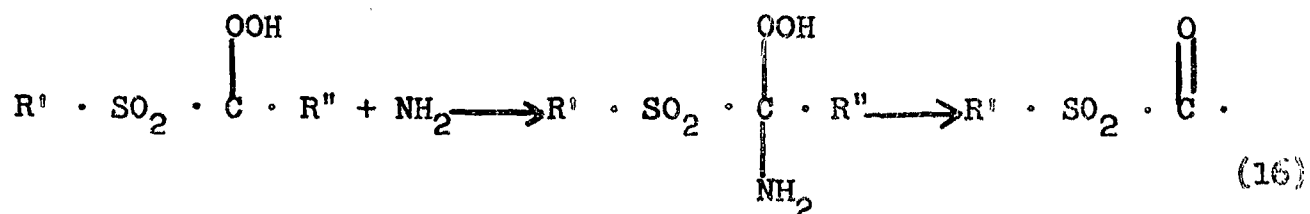
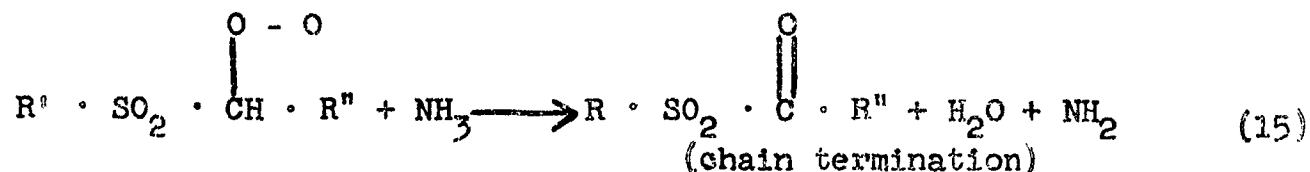
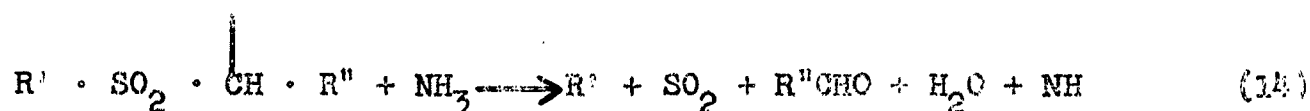
The sulfones are not attacked by peroxides, but molecular oxygen oxidizes them to sulfonic acids or even to  $\text{SO}_3$  (the latter especially at high temperatures):



That is, the formation of  $SO_3$  from the sulfides is facilitated if the sulfides are oxidized to sulfoxides or sulfones during the preflame period. The oxygen attacks the  $CH_2$  group adjacent to the  $SO_2$  group, because the former group has highly active hydrogen; this selective oxidation gives rise to  $SO_3$  even before the combustion of the fuel is complete, so the  $SO_3$  is present in the cylinder much longer than other products. In consequence, the  $SO_3$  has a high probability of being transformed to  $H_2SO_4$  at the cool walls of the cylinder, and the two compounds can react with the oil and with the other oxidation products as above.

This mechanism for the formation of  $SO_3$  implies that the process as a whole must be inhibited at its first stage (oxidation of the sulfides). It is likely that the sulfones, and peroxide radicals derived from them, are formed very largely during the high-temperature oxidation of the fuel droplets, so the treatment should take the lines of decomposing the peroxides (and radicals) in the vapor state. The ammonia reacts with the peroxides and peroxide radicals, and so prevents the sulfur from being oxidized to  $SO_3$ . A possible scheme of radical reactions for this process is as follows:





This scheme shows that the ammonia has several distinct effects. The NH and NH<sub>2</sub> radicals are active inhibitors for the vapor-phase oxidation of sulfones; they prevent the oxidative decomposition of the hydrocarbons. The function of the ammonia is analogous to that of an antiknock additive in gasoline, which would indicate that the addition of a powerful antiknock additive to sulfur-rich diesel fuel should produce a marked reduction in the SO<sub>3</sub> content of the exhaust gases. Direct tests demonstrate that this is so; the addition of 2 ml of R-9 (0.2% tetraethyl lead) to a fuel containing 1.57% of sulfur resulted in a threefold reduction of the SO<sub>3</sub> content of the exhaust gases from a 2Ch-8.5/11 engine (from 22 to 6 mg per 100 liters of exhaust). The proportion of SO<sub>2</sub> increased correspondingly.

This is a confirmation of the above scheme for the suppression of  $\text{SO}_3$  by ammonia; it also points an entirely new direction in studies on the use of sulfur-rich fuels.

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